

## Acid deposition and critical load analysis in Agra, India

Anindita Bhattacharya\*, Richa Mudgal, Ajay Taneja

Department of Chemistry, St. John's College, School of Chemical Sciences, Agra 282005, India

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### Abstract

The deposition of sulphur ( $161.1 \text{ eq. ha}^{-1}$  per year), nitrogen ( $49.9 \text{ eq. ha}^{-1}$  per year), and ammonium ( $176.8 \text{ eq. ha}^{-1}$  per year) from the atmosphere were calculated for both wet and dry deposition in Agra region of India. Seven sampling sites located at Bichpuri, Bah, Fatehabad, Shamsabad, Nunhai, Dayalbagh, and St. John's College were used. The values for critical load of sulphur and nitrogen for soil with respect to Hibiscus (*Hibiscus rosa-sinensis*) and Black siris (*Albizzia odoratissima*) were calculated. The methodology employed involved the steady state mass balance (SSMB) method. The values of actual acidity were compared with the RAINS-Asia model. On comparing the acidity, it was found that the values computed by RAINS-Asia model are higher for this area.

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### 1. Introduction

Air pollution is an emerging issue in Asia. In particular, emission of sulphur dioxide and nitrogen oxides have been rising steadily over the last few decades. Rapid growth of cities together with expansion of industries and transport systems has made the Asian region increasingly exposed to these emissions. Projections indicate that potentially large increases in emission may occur during the next 20–50 years if the current trend persists. If this occurs, the impacts that have been experienced in Europe will become apparent in large part of Asia. These problems include the reduction in crop yield by direct effects of gases, acidification of lakes [1], impacts on human health, impacts of corrosion on human made structures [2], impacts on soil fertility leading to damaging changes in natural ecosystem and impacts on forests and crop growth in sensitive soils [3]. Impacts are most visible on a local scale. With the rapid economic development, energy consumption of the world has increased significantly in the last decade. Coal consumption which acts as the main process of energy production, has generated large amount of acid precursors and has resulted in the acid deposition in

some areas of the world. Acid deposition affects the vitality of forest ecosystems both by direct effects on the forest canopy and by indirect soil mediated effects on the roots.

Both local and long-range emission sources contribute to atmospheric deposition of contaminants. This deposition is comprised of both dry and wet materials. The dry component consists mostly of dust particles contributed by natural sources such as soils, plant debris and volcanic emissions and anthropogenic sources like fertilizers, fly ash and other soil amendments. Wet deposition process is the major pathway for removal of pollutants from the atmosphere to the biosphere. It involves complex transformation of  $\text{SO}_2$  and  $\text{NO}_2$  to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in a cloud [4–7].

Concern about the undesirable effects of air pollution in many areas of northern hemisphere has led to considerable amount of national and international research into the impact of acid deposition on terrestrial and aquatic ecosystems. These often yield results that are not quantitative or regionally relevant. As a result, this information may be of little value to policy makers and resource managers. In order to facilitate the transfer of scientific information for policy decisions concerning emissions of air pollutants, the concept of critical loads and target loads have been developed.

For countries like India where dry conditions prevail for a major part of the year and precipitation is confined to a short rainy season, dry deposition is important. However, both small scale meteorological parameters at the time of

\* Corresponding author. Tel.: +91-512-257-46-79/259-77-59;

fax: +91-512-259-77-59.

E-mail addresses: anindi@iitk.ac.in, anib\_a@yahoo.com (A. Bhattacharya).

deposition and the nature of the collecting surface makes it difficult for an accurate estimation of dry deposition rates [4,8,9]. Hence, no uniformly accepted method has been developed to minimize this phenomenon although progress has been significant in the last 10 years. Surrogate surfaces have been widely used and they are potentially useful as they provide a common surface available for application in a wide variety of environments.

Thus, pollution is a necessary evil of all developments. Emphasis on a cost-effective strategy for pollution impact minimization based on scientific criteria has led to the development of the critical load concept. The critical load approach is a methodology according to which critical loads are used as the criteria to assess whether emission reduction strategies are sufficient.

The definition of critical loads adopted by the United Nations Economic Commission for Europe (UNECE) is a quantitative estimate of exposure to one or more pollutants below which significant harmful effects on sensitive elements of the environment do not occur [1,10]. The linking of the ecosystem response to deposition level is the critical principle of the critical load approach. In order to utilize the critical load concept, four elements [11] that need to be defined are receptor, biological indicator, chemical criterion, and critical limit. In this study a steady state mass balance (SSMB) method [12] was used to calculate the critical load of sulphur and nitrogen for soil from dry deposition in Agra region, India.

## 2. Materials and methods

### 2.1. Study area

This study considered the entire Agra region. Seven sampling sites located at Bichpuri, Shamsabad, Fatehabad, Bah, Nunhai, Dayalbagh, and St. John's College were employed. Agra (27°10'N, 78°05'E) lies in a semi arid zone adjacent to the Thar desert of Rajasthan. The soil of the district is alluvial except for residual soils occurring in a narrow strip in the south and south-west lower horizons of the region where it is sandy loam soil. The pH and conductivity of soil vary between 7.5 and 8.4 and 0.07–2.6 mS cm<sup>-1</sup>, respectively.

### 2.2. Sample collection

Sample collectors were approximately 8 m from the ground level and 1 m above the floor of the roofs. This distance was chosen to prevent contamination by splashes from the ground. Dry deposition samples were collected using the surrogate collection technique that employed passive polypropylene collectors. The general set up and procedure has been described by Mahadevan et. al. [13].

Manual sample collectors were made by attaching a funnel with an internal diameter of 14 cm to a polyethylene

bottle. The collectors were exposed for a period of 2 days. After this period, the deposition on the funnel was washed off at the site using deionised water, collected in the bottle and made up to 100 ml. The pH of the sample was determined immediately after collection. The samples were then filtered into two pre-cleaned polyethylene bottles. One aliquot was refrigerated for anion analysis and the other part was acidified with HNO<sub>3</sub> for cation analysis. Rain water was obtained using similar sample device.

Soil samples were also collected from the sampling sites for total nitrogen content analysis. Soil samples were collected in zigzag manner in the area. Soil samples were obtained by removing approximately 6 cm of soil from the surface. The soil samples were placed in polythene bags with the opening tied before transport to laboratory. The soil samples were ground, sieved through a 2 mm sieve and dried before analysis. Soil solutions were prepared by placing 10 g of soil in 25 ml of water, stirred well for 30 min, and filtered. The pH was determined immediately.

### 2.3. Analysis

The steady state mass balance method was utilized to determine the critical pollution load. SSMB is the most commonly used method for analysis of critical load of acid deposition. Its basic principle is based on identifying the long-term average sources of acidity and alkalinity in order to determine the maximum acid input that will balance the system at a bio-geochemical safe-limit [12]. Several assumptions have been made in the steady state calculations. First, it is assumed that ion exchange is at steady state and there is no net change in base saturation or no net transfer of acid neutralizing capacity (ANC) from soil solution to the ion exchange matrix. It is assumed that for nitrogen there is no net denitrification, adsorption or desorption and the nitrogen cycle is at steady state. Sulphate is also assumed to be at steady state, no sulphide oxidation, sulphate uptake, sulphate permanent fixation or sulphate reduction are significant. Simple hydrology is assumed where there is straight infiltration through the soil profile.

The critical load of actual acidity CL(Ac<sub>act</sub>) was computed by the method given by Hettelingh et al. [14]:

$$CL(Ac_{act}) = BC_w + [H]_{crit}Q + [Al]_{crit}Q \quad (1)$$

where BC<sub>w</sub>: weathering of the base cation (eq. ha<sup>-1</sup> per year), *Q*: runoff (eq. ha<sup>-1</sup> per year), [H]<sub>crit</sub>: critical hydrogen leaching (eq. m<sup>-3</sup>), [Al]<sub>crit</sub>: critical aluminium leaching (eq. m<sup>-3</sup>), where eq. ha<sup>-1</sup> per year is equivalent per hectare per year. The sulphur fraction is designed to compute the net contribution of sulphur (S) and nitrogen (N) to the critical load of actual acidity. The sulphur fraction (*S<sub>f</sub>*) is defined as follows:

$$S_f = \frac{PL(SO_x)}{PL(SO_x) + PL(NO_x) + PL(NH_x) - (N_u + N_i)} \quad (2)$$

Table 1  
Computed values of wet and dry deposition (eq. ha<sup>-1</sup> per year of sulphate, nitrate, and ammonium) at seven sampling sites in India

Sampling sites	Dry deposition					Wet deposition				
	Sulphate	as S	Nitrate	as N	Ammonium	Sulphate	as S	Nitrate	as N	Ammonium
Bichpuri	213.0	71.1	111.1	25.1	77.8	271.0	90.3	109.7	24.8	97.8
Bah	211.5	70.6	110.7	25.0	76.8	271.1	90.3	109.3	24.7	98.8
Fatehabad	212.1	70.8	111.3	25.1	77.1	270.8	90.2	109.4	24.7	99.1
Shamsabad	212.0	70.7	111.5	25.1	77.0	271.1	90.3	109.5	24.7	99.0
Nunhai	213.4	71.2	112.4	25.3	78.0	271.8	90.6	110.5	25.0	100.0
Dayalbagh	211.0	70.4	111.0	25.0	77.4	270.2	90.1	109.0	24.6	99.4
St. John's College	212.2	70.8	111.3	25.1	77.4	271.0	90.3	109.8	24.8	99.4
Average	212.2	70.8	111.3	25.1	77.4	271.0	90.3	109.6	24.8	99.1

Table 2  
Values used for [H]<sub>crit</sub>, [Al]<sub>crit</sub>, Runoff (*Q*), nitrogen immobilization (*N<sub>i</sub>*), and base cation weathering rate (BC<sub>w</sub>) for soil

[H] <sub>crit</sub> (eq. m <sup>-3</sup> )	[Al] <sub>crit</sub> (eq. m <sup>-3</sup> )	Runoff ( <i>Q</i> ) (eq. ha <sup>-1</sup> per year)	BC <sub>w</sub> (eq. ha <sup>-1</sup> per year)	<i>N<sub>i</sub></i> (eq. ha <sup>-1</sup> per year)
0.09 <sup>a</sup>	0.2 <sup>a</sup>	−3440	1430	0.009

<sup>a</sup> [14].

Table 3  
Calculated value of critical load of sulphur and nitrogen in soil

Common name	Botanical name	Nitrogen uptake (eq. ha <sup>-1</sup> per year)	Critical load for soil	
			Eq. (3)	Eq. (4)
Hibiscus	<i>Hibiscus rosa-sinensis</i>	2.133 [17]	180.7	253.8
Black siris	<i>Albizia odoratissima</i>	3.85 [18]	181.6	254.7

when  $PL(NO_x) + PL(NH_x) > (N_u + N_i)$ , otherwise  $S_f$  is equal to unity. Where  $PL(SO_x)$ : current load of sulphur (eq. ha<sup>-1</sup> per year),  $PL(NO_x)$ : current load of nitrogen (eq. ha<sup>-1</sup> per year),  $PL(NH_x)$ : current load of ammonium (eq. ha<sup>-1</sup> per year),  $N_u$ : nitrogen uptake for managed crops (eq. ha<sup>-1</sup> per year),  $N_i$ : nitrogen immobilization (eq. ha<sup>-1</sup> per year).

Critical loads of S and N were calculated using the following formulae:

$$CL(S) = S_f CL(Ac_{act}), \quad (3)$$

$$CL(N) = N_u - (1 - S_f) CL(Ac_{act}) \quad (4)$$

The weathering rate of the soil is 1430 eq. ha<sup>-1</sup> per year as calculated from the observed correlation between observed weathering rates and whole soil total content of magnesium and calcium [15]. Table 1 depicts the mean values of wet and dry deposition of sulphate, nitrate, and ammonium. The annual rainfall at Agra is 766 mm [16].

The critical load of actual acidity was calculated by substituting the values from Table 2 in Eq. (1). The value of the critical load of actual acidity was found to be 432.4 eq. ha<sup>-1</sup> per year. The calculated values of CL(S) and CL(N) using Black siris tree and Hibiscus are shown in Table 3. The critical acidity load was also determined by using RAINS-Asia model [12] for this region.

### 3. Results and discussion

It was found that the sulphur (161.1 eq. ha<sup>-1</sup> per year) and nitrogen (49.9 eq. ha<sup>-1</sup> per year) loads are much lower than the critical loads of S and N in the soil with respect to Black siris (*Albizia odoratissima*) and Hibiscus (*Hibiscus rosa-sinensis*). The value obtained for the actual acidity by using RAINS-Asia model is greater than the value calculated by using Eq. (1).

### 4. Conclusions and recommendations

The critical load approach, in combination with integrated assessment models has been utilized to some extent to guide European national policy formulations to reduce acidic emissions. Thus, the use of critical load values as indicators of deposition limits should enable some of the adverse effects encountered in the country to be avoided.

Deposition alone is not the only cause of increased risk of damage. Atmospheric concentrations (of SO<sub>2</sub>, NO<sub>x</sub>, and ozone) have been shown to cause direct damage to natural ecosystems and crops as well as having health effects. Interactions between pollutants are likely, such as acidity with heavy metals and the possibility of climate change and associated changes in cropping systems and vegetation land cover may add to the complexity.

Nevertheless, as a starting point, the RAINS-Asia model can be applied in combination with the critical load approach to support policies which are aimed at reducing acidic emissions such that the excess of critical loads can be controlled. This analysis will be able to anticipate pollution risks to a particular receptor.

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